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COMPLETE SPECIFICATION

Improved Crystalline Zeolites and method of preparing same

We, MOBIL OIL CORPORATION, A Corporation organised under the laws of the State of New York, United States of America, of 150, East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for preparing crystalline aluminosilicates.

The desirability of achieving by base exchange as low a sodium content as possible in crystalline aluminosilicates which are eventually to be employed as catalysts is well known to the art, for instance from U.K. Specification No. 1,000,901. It is also known, for instance from U.K. Specification No. 1,058,762, that where the catalysis in question is of the cracking of hydrocarbon oil to produce hydrocarbons of lower boiling range the incoming ion by which sodium is replaced in such base exchange is advantageously rare-earth.

The present invention is of general application to those methods of producing crystalline aluminosilicates destined ultimately to be used as catalysts which involve the elimination from the starting aluminosilicate of originally-present mono- or divalent cations and the introduction into the aluminosilicate of cations e.g. trivalent cations. We have encountered, in the practice of such methods, difficulty in realizing a final product having as low a content of the mono- or divalent cations as we should expect having regard to the extent of the base exchange to which we had subjected the starting material for the purpose of removing them; and we have also observed that the final product in some cases contains a lower content than we had expected of the cation e.g. trivalent cation introduced, having regard to similar considerations, and that the degree of crystallinity of the final product is in some cases seriously reduced, particularly in those instances where flash drying is employed as a stage in the preparation.

The first of these difficulties now appears to us to be a consequence of the fact that a minor proportion of the original monovalent or divalent cation, e.g. alkali-metal cation or alkaline earth metal cation — usually sodium — of the crystalline aluminosilicate is associated with the basic silicon-oxygen-aluminum lattice in a manner slightly different from that in which the major proportion is associated, the difference being of a kind which renders the minor proportion resistant to removal by base exchange relative to the major: that minor proportion may therefore remain in the aluminosilicate after a base-exchange operation of extent which would justifiably be expected to remove the whole of the cation were the whole of that cation associated with the lattice in the same manner.

The second difficulty can likewise be traced to the manner of association between the incoming cation e.g. trivalent cation — often rare earth — and the lattice. We have found that rare earth ions, the presence of which in a crystalline aluminosilicate tends to impart to the aluminosilicate resistance to conditions which might otherwise cause the crystalline material to degrade to the amorphous condition, are capable of relatively strong or relatively weak association with the lattice. The diminished content of rare earth cation in the final product is therefore assumed to follow from the creation only of the relatively weak association with the lattice when these cations

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are introduced by base exchange, with the result that subsequent steps in the overall preparation may cause severance of that association thus lowering both the rare earth content itself and also the resistance to loss of crystallinity of the aluminosilicate.

We have found that at least part of that portion of mono- or divalent cation which is resistant to removal by base-exchange may be rendered easily so removable if the crystalline aluminosilicate containing it is heat-treated.

The present invention provides a method of preparing a crystalline aluminosilicate for use as a catalyst, comprising heating an aluminosilicate containing mono- and/or divalent cations to a temperature in the range 150 to 1700°F. for a time sufficient to reduce the moisture content of the aluminosilicate to less than 90% of saturation and thereafter subjecting the aluminosilicate to base-exchange to reduce the content of said mono- and/or divalent cations to less than 80% of their content prior to said base-exchange.

The invention is accordingly characterised by the fact that before base-exchange, e.g. with trivalent metal cations, to remove the resistant portion is attempted the aluminosilicate is heated to a temperature in the range 150 to 1700°F., preferably to a minimum temperature of 250°F., even more preferably to a temperature in the range 1200 to 1400°F., the time for which the material must be held at the heating temperature corresponding to the time required at that temperature to reduce the moisture content of the aluminosilicate below 90%, preferably below 70% and even more preferably below 20%, of the saturation value.

The monovalent cations may be alkali metal cations, e.g. sodium ions. The sodium ions may have resisted removal in a prior base-exchange, which, for example, replaced sodium ions by rare earth ions. The base-exchange subsequent to the heating may also replace sodium ions by rare earth ions.

The aluminosilicate starting material may contain trivalent cations, in addition to the mono- and/or divalent cations, before being heated. Indeed a substantial proportion of the cations in the aluminosilicate may be rare earth cations.

We have also found that, provided the heating is conducted above a certain minimum temperature, it achieves the further effect of strengthening the bonding to the lattice of trivalent cation present: a preferred embodiment of the invention is therefore characterised by the fact that the heating of a crystalline aluminosilicate which has previously been subjected to base-exchange to introduce trivalent cation, particularly rare earth, is carried out in the range 250 to 1700°F. The product of the preferred embodiment has enhanced resistance to loss of crystallinity or of rare earth cation, and, in particular, may be processed by the flash-drying technique whilst retaining crystallinity.

The aluminosilicate may be heated in an atmosphere of steam, air-steam, nitrogen, flue gas, oxygen or hydrogen. After the base-exchange subsequent to the heating, the aluminosilicate may be once more subjected to the heating followed by the base-exchange.

The base-exchange of the aluminosilicate subsequent to heating may reduce the alkali metal content of the aluminosilicate to a value within the range 0.03 to 0.2 weight percent.

The aluminosilicate subjected to base-exchange subsequent to heating may be mixed with relatively catalytically inert material. For example the aluminosilicate subjected to heating is mixed with the relatively catalytically inert material. Alternatively the aluminosilicate subjected to base-exchange prior to heating may be mixed with relatively catalytically inert material.

After the final base-exchange the aluminosilicate may be spray-dried.

Trivalent metal cations which may be fixed in the zeolite in accordance with our invention include the rare earth metals, i.e. metals having atomic numbers in the range 57 to 71, yttrium, scandium, manganese, iron, chromium, ruthenium, rhodium, gold, indium, gallium, and aluminium, with preference being accorded the rare earths and yttrium.

Suitable cations which may be introduced into the zeolite by ion exchange (after the zeolite has been subjected to thermal treatment to effect redistribution of the monovalent and/or divalent cations present therein) at the expense of one or more of the foregoing monovalent and/or divalent cations include ammonium, rare earth, beryllium, calcium, magnesium, as well as other metal cations from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVB, VIB, VIIB, and VIII of the "Periodic Table of the Elements," (1962), distributed by E. H. Sargent & Co., Chicago, Illinois.

Other advantages, characteristics, and features of our invention will become apparent from the following detailed description, given by way of example, taken in conjunction with the accompanying drawings wherein:

Fig. 1 is a graph showing relative crystallinities for rare earth aluminosilicates heat treated in accordance with our invention;

Fig. 2 is a graph showing relative amounts of residual sodium present in rare earth aluminosilicate, heat treated and ion exchanged in accordance with our invention;

Fig. 3 is a graph showing relative rare earth retention after ion exchange for rare earth aluminosilicates which were heat treated, in accordance with our invention, prior to such ion exchange; and

Fig. 4 is a graph showing relative crystallinities after treatment with various acidic solutions for rare earth aluminosilicates which were heat treated, in accordance with our invention, prior to such acidic treatment.

The trivalent metal cation containing aluminosilicates, e.g., rare earth aluminosilicates, are prepared by base exchanging an alkali metal aluminosilicate which has a uniform pore structure comprising openings characterized by an effective pore diameter of greater than 3, preferably greater than 5, and most preferably between 6 and 15 Angstroms. The alkali metal aluminosilicate may be of the A-type, X-type, Y-type, L-type, D-type, T-type, K-G type, mordenite type, or other well known form of molecular sieve, and can be prepared following the general procedures described in U.S. patent 2,882,243 (A-type); U.S. patent 2,882,244 (X-type); U.S. patent 3,130,007 (Y-type); German patent 1,100,009 (L-type); German patent 1,009,511 (D-type); U.S. patent 2,950,952 (T-type); U.S. patent 3,056,654 (K-G type). The aluminosilicates may also be those which occur naturally such as mordenite, chabasite, gmelinite, offretite (erionite), neulandite, clinoptilolite, and stilbite.

Base exchange of the alkali metal aluminosilicates is generally effected by treatment with a solution characterized by a pH in excess of about 4.5, preferably by a pH in the range of 5 to 10, and containing the cations to be exchanged into the aluminosilicate.

The degree of exchange that will be achieved differs for the various zeolites. Thus, for zeolite X conventional ion exchange proceeds reasonably rapidly until about 0.1 equivalent of alkali metal remains per equivalent of Al in the lattice; for zeolite Y having a silica-alumina molar ratio of 6 conventional exchange is rapid until about 0.25 equivalent of alkali metal per equivalent of Al remains; for alkali metal mordenite, exchange proceeds until about 0.5 equivalent of alkali metal remain per equivalent of Al.

The lowest pH that can be utilized for the base exchange solution is governed by the mole ratio of silica to alumina of the crystalline lattice of the aluminosilicate. For silica-alumina mole ratios below about 4 the lowest pH is generally limited to about 4.5. For silica-alumina mole ratios from about 4 to 8 the lowest pH is about 2. For silica-alumina mole ratios above 8, the pH may be 1 or even lower.

The alkali metal content of the finished base-exchanged aluminosilicate sieve is therefore desirably less than about 0.8 equivalent per equivalent of Al in the zeolite lattice, preferably is less than 0.6 equivalent per equivalent of Al in the lattice, and most preferably is less than 0.3 equivalent per equivalent of Al in the lattice. Thus, the base exchange is generally carried out for a sufficient period of time and under appropriate temperature conditions to replace at least 40 per cent of the exchangeable cations, e.g. alkali metal, originally contained in the aluminosilicate.

Any soluble compound of trivalent metal, e.g., rare earth metal, may be employed for base exchange. Generally, an aqueous solution of a trivalent metal salt, typically a rare earth metal salt or mixture of rare earth metal salts is employed. Thus, the rare earth metal salt (or salt of another trivalent metal) may be a chloride, sulfate, nitrate, formate or acetate. The metal cation may be cerium, lanthanum, praseodymium, neodymium, samarium, or other rare earths, as well as scandium or yttrium. Solutions containing mixtures of these ions and mixtures of the same with other ions, such as ammonium may be employed. In such latter instance the aluminosilicate will contain not only trivalent metal cations but will also contain ammonium cations. When such a trivalent metal aluminosilicate, e.g., rare earth aluminosilicate, is heated, ammonia is liberated to thereby leave hydrogen, so that the resultant aluminosilicate contains hydrogen cations as well as trivalent metal cations. In those zeolites which have openings large enough to accommodate large ions, alkyl ammonium ions such as methyl ammonium ion, dimethyl ammonium ion, trimethyl ammonium ion and tetramethyl ammonium ion may be used in place of ammonium cations.

It is contemplated that such trivalent metal hydrogen aluminosilicates, e.g., rare earth hydrogen Y aluminosilicates, may be employed in the present invention, and the expression "trivalent metal aluminosilicate" is intended to include aluminosilicates containing, in addition to trivalent metal cations, other cations such as hydrogen and ammonium.

While water will ordinarily be the solvent in the base-exchange solutions used, other solvents may also be used, e.g., alcohols.

The concentration of compound employed in the base-exchange solution the cation of which is to be exchanged and the quantity of solution employed may vary depending on the nature of the particular compound used, on the alkali metal aluminosilicate undergoing treatment and on the conditions under which treatment is effected. The overall quantity and concentration of the replacing cation, however, is usually more than theoretically required to remove all of the sodium metal content of the original alkali metal aluminosilicate. We have found, however, that conventional ion exchange does not remove all of the sodium cations, even when two and three fold excesses of replacing cations are employed. Generally, the concentration of compound, the cation of which replaces cations originally present in the aluminosilicate, is within the range of 0.1% by weight to saturation.

The temperature at which base exchange is effected may vary widely, generally ranging from ambient temperature to an elevated temperature below the temperature at which the crystallinity of the aluminosilicate is destroyed by the treating solution. Preferably the exchange is carried out at temperatures between about 50 and 700°F. The volume of base-exchange solution employed generally is such that an excess is employed, such excess being removed after a suitable period of contact. The time of contact between the base-exchange solution and crystalline aluminosilicate desirably is such as to effect replacement of the cations originally present in the aluminosilicate, e.g., alkali metal ions, to an extent such that the content of such original cations in the zeolite, after base exchange, is less than 0.6 equivalent per equivalent of Al in the zeolite. Such period of contact may vary widely depending on the temperature of the solution, the nature of the aluminosilicate used, and the particular compound employed for base exchange. Thus, the time of contact may extend from a brief period of the order of a few minutes for small particles of some zeolites to longer periods of the order of months for large crystals. After base-exchange treatment, the product is removed from the treating solution. It is desirable to remove soluble ions introduced as a result of treating with the base exchange solution, and this is readily effected by water-washing. Also, multiple contacts between zeolite and base exchange solutions may be carried out according to well known countercurrent and co-current methods. Conditions are adjusted to give the above designated degree of exchange.

In accordance with one aspect of our invention, a trivalent metal aluminosilicate zeolite is subjected to a heat treatment in order to render the trivalent metal ions resistant to further exchange, to render the crystals resistant to treatment with acids and acid salt solutions, and to render the crystals stable when spray dried. The heat treatment should desirably be carried out under such temperature and time conditions as to produce a product having a residual moisture content not greater than 6 per cent by weight (zero to 6 per cent), desirably from about 0.3 to 6 per cent, preferably from about 1.5 to 6 per cent, and most preferably from about 1.5 to 3 per cent by weight. The temperature at which such heating may be carried out should be from 250 to 1700°F., and preferably from about 600 to 1700°F. Of course, the higher the temperature, the less the time required at such temperature to effect the desired degree of dehydration. Accordingly, whereas many days of heating in dry air may be required at 250°F., several minutes of heating may suffice at temperatures of about 600°F., and only a few milliseconds will be required at a temperature at or near 1700°F. Of course, where such elevated temperatures are employed the magnitude of the temperature and/or the time duration must not be so great as to destroy the crystallinity of the zeolite.

By virtue of the foregoing heat treatment the trivalent metal ions are "fixed" in the zeolite crystal so that such ions are much more resistant to removal by ion exchange techniques than would be the case for a similar zeolite which was not subjected to the aforesaid heat treatment. Additionally, the heat-treated zeolite may be subjected to later processing with acidic solutions without adversely affecting either the characteristic zeolite structure or the catalytic activity of the zeolite.

Where such heat treated aluminosilicates are subjected to a wet processing step utilizing an acidic solution, the solution pH that is tolerable will depend on both the silica to alumina mole ratio of the zeolite and also to its alkali metal content. For rare earth faujasite of silica to alumina molar ratio of 2.5 and a sodium level of 1.3 wt%, solutions of 2 pH can be tolerated. The same type of crystalline material with 4% Na can tolerate only a 2.8 pH exchange solution. The pure sodium form of this zeolite is rendered amorphous by solutions of this pH. Rare earth mordenite which has a silica to alumina molar ratio of 10 can tolerate exchange solutions of at least 1 pH. In these cases there are no deleterious effects on the rare earth zeolite. Typical acidic solutions which may be employed in such wet processing include aqueous mineral acids such as sulfuric acid, nitric acid, hydrochloric acid, perchloric acid, acetic acid, and acid salt solutions such as aluminum sulfate, aluminum chloride, ferric sulfate, ferric chloride, chromium nitrate, zirconium sulfate and titanium sulfate.

Another advantage deriving from the foregoing heat treatment is that the resultant zeolite may be spray dried. Whereas such a zeolite that has not been heat treated will, upon spray drying, show a drastic reduction in its crystallinity and may actually become entirely amorphous, upon spray drying a zeolite which has been heated treated we have found that there is no appreciable reduction in the crystallinity of the zeolite. Spray drying is generally effected by spraying the aluminosilicate or a mixture of aluminosilicate and hydrogel into a hot air stream, e.g. at 1000°F. or higher. The evaporative cooling of the water lowers the temperature of the system. The temperature of the dried product is usually from about 200 to 500°F.

In accordance with another aspect of this invention, we have found that a crystalline aluminosilicate zeolite, which zeolite will typically contain from 1 to 5% by weight of residual alkali metal, can be subjected to a heat treatment followed by ion exchange with a solution containing cations which are desired to be introduced into the zeolite, whereby such cations are introduced into the zeolite at the expense of the residual alkali metal ions. It is believed that the heat treatment effects a redistribution of the alkali metal ions present in the zeolite. As a result of this redistribution, the alkali metal ions are rendered susceptible to ion exchange with the cation containing exchange solution.

It is frequently advantageous to water wash the crystalline zeolite prior to calcination and ion exchange. Such water washing serves to remove water-soluble ions and hence is desirable, but not essential.

In the foregoing embodiment, the temperature and time of the heat treatment may vary within wide limits. Thus, temperatures as low as 150°F may be employed. However, a time of up to several months may be required at such relatively low temperature. Alternatively temperatures as high as 1700°F may be employed, but in such instance the time is quite short, of the order of a few milliseconds. The upper temperature limit is, as in the preceding embodiment, controlled by that temperature at which the zeolite tends to lose its crystallinity.

The conditions of calcination should be sufficient to reduce the moisture content to less than 90% of saturation value. Saturation value is the amount of water necessary to completely fill the pores of the zeolite but does not include any water between crystallites. It is preferable that the moisture not exceed about 70% of saturation value, and most preferable that it not exceed about 20% of saturation value.

The foregoing heat treatment is desirably effected by thermal treatment in air, steam, air-steam, or any other medium that does not adversely affect the zeolite, e.g., an inert gas such as nitrogen, flue gas, oxygen or hydrogen. The thermal treatment is conveniently carried out at atmospheric pressure although, of course, greater or lesser pressures may also be employed.

To further reduce the residual alkali metal content of the zeolite, the thermally treated zeolite is subjected to ion exchange. It is desirable that from 0.05 to 0.2 equivalent of alkali metal per equivalent of Al in the zeolite structure be exchanged out.

The ion exchange may be effected on the "pure" zeolite. Thereafter, the zeolite, now depleted in alkali metal content, may be used as a catalyst, e.g., in a fluidized bed, as pressed pellets or bound extrudates in fixed or moving beds, or as the active catalytic component in a composite made up of such zeolite dispersed in a porous matrix. The matrix may be made up of an inorganic oxide, e.g., silica-alumina or clay, or of metal salts, e.g., barytes. The clay may be untreated or acid leached.

Alternatively, the sequence can be altered. Thus, a catalyst composite may be prepared by first dispersing the thermally treated zeolite (prior to ion exchange) throughout a porous inorganic oxide matrix, and then subjecting such composite to

ion exchange treatment whereby the cations present in the ion exchange solution enter into the composite at the expense of residual alkali metal present (1) in the matrix and (2) in the dispersed zeolite.

The thermal treatment of the crystalline aluminosilicate zeolite renders the residual alkali metal therein much more accessible to ion exchange and hence, much more easy to remove. Thus, subsequent ion exchange affords an aluminosilicate zeolite containing less than 80% of the quantity of alkali metal that it contained after calcination but prior to ion exchange, preferably less than 75% of such quantity, and in many instances less than 50% of such quantity. Indeed, a residual alkali metal content within the range of from about 0.03 to 0.2 weight per cent of the zeolite is readily obtained. When considering a composite made up of a porous matrix containing previously heated aluminosilicate zeolite dispersed therein, ion exchange of such composite results in a residual alkali metal content of less than about 0.2 weight per cent by weight of the composite, and typically from about 0.05 to 0.15 per cent.

Where the crystalline zeolite is to be dispersed in a porous matrix, it is to be understood that other finely divided material may also be dispersed in this same matrix, e.g., siliceous oxide fines, high density alpha alumina fines, lower density materials such as recycle catalyst fines and uncalcined clay. Other materials include those disclosed in U.S. Patent 2,900,349. The optimum fines size and concentration will vary depending upon the particular material used. In general, however, the particle size of the fines should be from about 0.1 to 40 microns weight mean particle diameter.

Suitable matrix materials include silica gel, cogels of silica and a metal oxide, clay, activated carbon, metal salts and metals. Where a cogel of silica and a metal oxide is employed as the matrix, the metal may be one or more of those metals of Groups II, IIIA, IVB and VIB of the Periodic Table. Suitable cogels include, for example, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary combinations such as silica-alumina-thoria, silica-alumina-chromia, silica-alumina-zirconia, silica-alumina-titania, silica-alumina-beryllia, silica-alumina-magnesia and silica-magnesia-zirconia. The silica content of the silica-metal oxide gel matrix will generally be within the approximate range of 75 to 99 weight per cent with the metal oxide ranging from about 1 to about 25 weight per cent.

An alkali metal silicate reactant is employed to prepare the silica-metal oxide matrix. This reactant is generally sodium silicate but other alkali metal silicates, e.g., potassium silicate, may likewise be used. The concentration of alkali metal silicate solutions employed in the present process is generally such that the silica content thereof is between about 5 per cent and about 30 per cent by weight.

Generally a slurry of finely divided dehydrated rare earth aluminosilicate is formed and is added to the alkali metal silicate solution, along with an acidic solution which may contain one or more metal salts, as described above, the oxides of such metals being cogelled with silica. The acidic solutions used in gelation can include sulfuric acid, hydrochloric acid, nitric acid and acetic acid, in which is mixed one or more metal salts such as aluminum sulfate, aluminum chloride, aluminum nitrate, zirconium sulfate, titanium tetrachloride, magnesium sulfate and chromium sulfate. There results a hydrosol which sets rapidly to a hydrogel, which hydrogel consists of silica-metal oxide matrix in which is dispersed finely divided aluminosilicate zeolite.

As noted, other fines may also be dispersed in the silica-metal oxide gel matrix, e.g., siliceous oxide gel fines made of silica gel or the silica-metal oxide cogels described above, metal oxide fines made of alumina or kyanite. Of course, any such fines shall be substantially free of materials which may poison the hydrocarbon conversion process. For example, the presence of various metals such as nickel, vanadium, iron or sodium, in specific amounts are known to adversely effect hydrocarbon conversion of hydrocarbon oils. Fines which contain these poisons should be avoided.

The crystalline aluminosilicate zeolite-inorganic oxide product may be prepared in any desired physical form. Thus, the sol containing added finely divided crystalline aluminosilicate may be permitted to set in mass to a gel which is thereafter dried and broken into pieces of desired size. The pieces of dried gel so obtained are generally of irregular shape. Uniformly shaped pieces of dried gel may be obtained by extrusion or pelleting of pulverized aluminosilicate-containing gel with a suitable binder such as bentonite clay. Also, the hydrosol may be introduced into the perforations of a perforated plate and retained therein until the sol has set to a gel, after which the formed gel pieces are removed from the plate. It is frequently desirable that the catalyst be in the form of spheroidal particles. The sol containing powdered aluminosilicate may be made into spheroidal particles by any feasible process, such

as methods described in patents to Marisic, for example, U.S. 2,384,946. Broadly, such methods involve introducing a sol into a column of water-immiscible liquid where it breaks into globules; for example, an oil medium wherein the sol breaks into globules, sets to a gel and the globules subsequently pass into an underlying layer of water from which they are sluiced to further processing operations such as base exchange, water-washing, drying and calcining. Larger size spheres are ordinarily within the range of from about 1/64 to about 1/4 inch in diameter, whereas smaller size spheres, which are generally referred to as microspheres, are within the range of from about 10 to about 100 microns in diameter. The use of the spherically shaped particles is of particular advantage in hydrocarbon conversion processes, including the moving catalyst bed processes and the fluidized process, in which the spheroidal gel particles are subjected to continuous movement. As applied to the stationary bed, spheroidal catalyst particles provide effective contact between the reactants and the catalyst by avoiding channeling.

On forming the crystalline zeolite-metal oxide composite a substantial amount of sodium or other alkali metals provided by the alkali metal silicate are present in the resulting composite. To remove the alkali metals and especially sodium, the composite is usually base exchanged, generally with a solution containing ammonium ions. This base exchange is effected by treatment with a suitable ammonium solution such as ammonium chloride, ammonium sulfate and ammonium acetate, desirably characterized by a pH in excess of about 4.5, preferably by a pH in the range of 5 to 10. The base-exchange operation is continued until the finished catalyst contains sodium metal of below about 0.4 weight per cent, desirably below about 0.2 weight per cent, preferably less than about 0.12, and most preferably less than about 0.10 per cent by weight. The time of the base-exchange contact may extend from a brief period of the order of a few hours for small particles to longer periods of the order of days for large pellets.

Rather than the foregoing base exchange with ammonium ions, the aluminosilicate zeolite (or the composite containing such zeolite dispersed therein) may be exchanged with a solution containing metal cations, e.g., rare earth ions, aluminium ions, calcium ions, thereby removing residual alkali metal and replacing it with such metal cations. Or the ion exchange may be effected using a solution containing several cations, e.g., ammonium ions and rare earth ions. It may be desirable to utilize a series of exchange treatments, e.g., with rare earth ion solutions and/or with ammonium ion solutions. In any event, the comparative ease with which residual alkali metal in the aluminosilicate zeolite is replaced with cations from the particular ion exchange solution is believed to be attributable to the initial thermal treatment of the zeolite.

Inasmuch as thermal treatment of a trivalent cation-containing crystalline aluminosilicate renders it resistant to low pH salt solutions, alkali metal present may be exchanged using low pH solutions rather than using such higher pH solutions as, e.g., rare earth salt solutions and/or ammonium salt solutions. For instance, there may be employed aluminium salt solutions having a low pH of about 3.8, or acid solutions such as acetic acid or about 2.8 pH or sulfuric acid of about 1.0 pH.

Generally water is employed as the solvent in the ion exchange solution. However, other solvents, while usually less preferred, may also be used. Thus, in addition to aqueous solutions, alcoholic solutions, of suitable compounds as previously described may be employed for the base-exchange treatment.

The concentration of compounds employed in the ion exchange solution will vary, depending on the nature of the particular compound or compounds used and upon the particular conditions under which the treatment is effected.

Generally the concentration of solute in the ion exchange solution is within the range of 1 to 15 per cent by weight, a more preferred range being from about 1 to 10 per cent by weight, a particularly desirable range being from about 1 to 3 per cent by weight.

The temperature at which ion exchange is effected may vary within wide limits, generally ranging from ambient temperature to an elevated temperature below the boiling point of the treating solution. The volume of ion-exchange solution employed may also vary widely, but generally an excess is employed, and such excess, after a suitable period of contact, is removed. Naturally the duration of such period of contact may also vary widely depending upon the temperature of the solution and the particular compound or compounds employed for base exchange. Accordingly, the contact time may be for a relatively brief period of the order of a few hours, or may extend for longer periods of the order of several days.

Thereafter the treating solution is removed from the product. Anions introduced as a result of treating with the ion exchange solution are removed by water washing.

The washed product is then dried in superheated steam to remove substantially all the water therefrom. The drying may be effected at ambient temperature in air, but it is preferred to dry at a temperature of from 260 to 340°F. for from 2 to 24 hours or even longer in superheated steam.

Where the foregoing zeolite is incorporated in an inorganic oxide matrix to form a composite suitable for cracking, such composite is generally subjected to a treatment so as to render it more attrition resistant and catalytically selective. Such treatment entails heating the composite in an atmosphere which does not adversely affect the catalyst such as steam, air, nitrogen, hydrogen, flue gas, helium or other inert gas. Generally, the dried composite is heated in steam or steam-air mixture to a temperature in the approximate range of 500°F. to 1500°F. for a period of at least about 1 hour and usually between 1 and 48 hours. The finished catalyst product has a surface area, within the approximate range of 50 to 400 square meters per gram.

If desired, the zeolite which has been heat treated in accordance with our invention may be incorporated in a fluid catalyst system. Such a fluid catalyst may be prepared, for example, by diluting sodium silicate with an equal volume of water, adjusting the pH to about 10 with aqueous sulfuric acid, ageing, adding sufficient aluminium sulfate solution to produce a pulp containing the equivalent of about 1 part by weight of alumina per 9 parts of silica, and adding concentrated ammonium hydroxide to raise the pH to about 8. The calcined treated aluminosilicate is then added. (Alternatively the calcined aluminosilicate may be added earlier, i.e., to the sodium silicate-water-sulfuric acid.) The material is then spray dried, followed by exchange with a dilute ammonium sulfate solution to reduce the sodium content to less than about 0.2 per cent by weight.

Cracking, utilizing the catalysts described herein, may be carried out at catalytic cracking conditions employing a temperature within the approximate range of 700°F. to 1200°F. and under a pressure from sub-atmospheric pressure up to several hundred atmospheres. The contact time of the oil within the catalyst is adjusted in any case according to the conditions, the particular oil feed and the particular results desired to give a substantial amount of cracking to lower boiling products. Cracking may be effected in the presence of the present catalyst utilizing well known techniques including, for example, those wherein the catalyst is employed in a fixed bed, as a compact particle-form moving bed, and as a fluidized bed of particles.

The cracking activity of the catalyst is a measure of its capacity to catalyze conversion of hydrocarbons and is expressed herein as the percentage conversion of a Mid-Continent Gas Oil having a boiling range of 450 to 950°F. to gasoline having an end point of 410°F. For bead or pelleted catalyst, the vapors of the said gas oil are passed through the catalyst at 875°F., at substantially atmospheric pressure and at a feed rate of 3 volumes of liquid oil per volume of catalyst per hour for ten minute runs between regenerations.

The following examples will further illustrate our invention. All parts are by weight unless otherwise stated.

EXAMPLE 1

This Example illustrates the preparation of a zeolite starting material for the crystalline aluminosilicates of the present invention.

A crystalline sodium aluminosilicate of the X-type having uniform pore openings between six and fifteen Angstrom units and used as starting material to prepare rare earth aluminosilicate, was prepared according to the procedure described in U.S. Patent No. 2,882,244. The sodium aluminosilicate was base exchanged by the addition of an aqueous solution containing 4 weight per cent rare earth chloride containing as its principal constituent cerium chloride, along with the chlorides of praseodymium, lanthanum, neodymium, and samarium. The amount of 4 per cent rare earth chloride solution used was 1.67 pounds for each pound of sodium aluminosilicate per base exchange. Twelve one-hour base-exchange treatments were conducted at solution temperatures of from 180 to 200°F. The resulting rare earth aluminosilicate was washed free of soluble salts and was ball milled to reduce its size to approximately four microns. The rare earth aluminosilicate product, rare earth zeolite X (REX) contained 26.5 weight per cent rare earth oxides (RE_2O_3) and 1.3 weight per cent sodium on a dry basis. The silica : alumina mole ratio was 2.5.

EXAMPLES 2-6

Samples of the material made as described in Example 1 were dried for 48 hours at 250°F. The dried powder was placed in a tray as a 1/8" thick layer. The sample was then placed in a preheated furnace chamber in a steam atmosphere and heated for 1 hour at the desired temperature. Chamber pressure was one atmosphere. Temperature was measured by a 1/16" diameter thermowell running parallel to the bottom of the tray through the center of the powder layer. Separate samples were heated (calcined) in this manner for 1 hour at 400°F, 650°F, 800°F, 1100°F, 1400°F and 1500°F. Approximately one half hour was required for the sample to reach the desired temperature. The sample, after removal from the furnace chamber, quickly cooled to ambient temperature. In each case the heating brought about removal of well in excess of 10 percent of the water in the zeolite.

The crystallinity, exchangeability of residual sodium, fixation of rare earth ions and stability of the heated (calcined) faujasite in acid solutions were all investigated with these samples.

X-ray crystallinities were determined. Samples were analyzed as they were taken from the furnace without any additional heating. After contact with solutions, samples were dried at 650°F before X-ray analysis. Cyclohexane adsorption tests were run on samples that had been heated (calcined) for 2 hours at 650°F.

In the ion exchange and acid stability tests, 10 grams of the heated (calcined) sample were agitated for 24 hours with 100 ml of solution at ambient temperature. Samples were then washed and then dried for 2 hours at 650°F before analysis. One normal NH_4Cl , $\text{Al}_2(\text{SO}_4)_3$, HCl , CeCl_3 and 0.26 normal $\text{Al}_2(\text{SO}_4)_3$ solutions were used.

The X-ray crystallinities, cyclohexane adsorptions, and rare earth oxide contents were plotted as dependent variables in Figures 1 through 4 as reduced values. The sample calcined at 800°F was taken as the base for calculating reduced values of crystallinity. The data from which these reduced values were calculated are given in Table 1.

Discussion of Results

Crystallinity

Samples which were calcined at temperatures up to 1400°F retained most of their crystallinity. Some loss in crystallinity did occur above 1000°F, however. At 1500°F the crystalline material became amorphous. These results are shown in Figure 1. This Figure gives the crystallinities of the materials used in all other tests described below.

Crystallinity was measured two ways: first, by the height of the peak in the X-ray powder pattern from CuK_α -radiation at 23.1° Bragg angle 2θ ; second, by adsorption capacity for cyclohexane at 20 mm cyclohexane partial pressure.

When the samples are calcined above 650°F, the crystallinities measured by X-ray analysis and by cyclohexane adsorption are about equal. Below 650°F the X-ray analysis gives lower crystallinities than cyclohexane adsorption due to a change in structure as REX is dehydrated. It is not caused by a change in the amount of crystalline material in the sample as is evidenced by the high cyclohexane adsorption capacity of the dried samples.

The increase in cyclohexane adsorption between 650°F and 800°F is probably caused by greater dehydration, and therefore, greater adsorption capacity, for samples originally calcined above 650°F.

Removal of Residual Sodium by Ion Exchange; Single Stage Exchange

After calcining the sodium becomes more easily exchangeable. This is shown in Figure 2 and in Table 1, Example 3. However, after 1500°F calcination, the crystal collapsed to amorphous material, and no sodium could be exchanged out of the amorphous solid.

TABLE 1
Analyses of Products

Example Number	2	3	4	5	6
Calcination Condition	Before Treatment with Solution	After Treatment with 1 Normal $\text{NH}_4\text{Cl}^{(1)}$	After Treatment with 1 Normal $\text{HCl}^{(1)}$	After Treatment with 1 Normal $\text{Al}_2(\text{SO}_4)_3^{(1)}$	After Treatment with 0.26 Normal $\text{Al}_2(\text{SO}_4)_3^{(1)}$
400° F., 1 Hr., in Steam, Atmospheric Pressure					
RE_2O_3 , % Wt.	26.5	21.2	14.4	12.9	21.4
Cyclohexane Ads., g/100 g	14.6	15.7	9.8	7.0	11.2
% Cryst. $^{(2)}$	120	160	20	10	120
% Shift	0	15	50	0	25
Na, Wt. % $^{(3)}$	1.3	0.61	0.24	—	.45
650° F., 1 Hr., in Steam, Atmospheric Pressure					
RE_2O_3 , Wt. %	20.5	28.5	21.2	23.8	25.4
Cyclohexane Ads., g/100 g	14.5	15.0	12.6	13.2	12.7
% Cryst. $^{(2)}$	175	170	140	160	160
% Shift	15	0	10	15	10
Na, Wt. % $^{(3)}$		0.29			
800° F., 1 Hr., in Steam, Atmospheric Pressure					
RE_2O_3 , Wt. %	26.5	27.3	21.3	24.0	25.8
Cyclohexane Ads., g/100 g	15.4	15.5	13.1	14	13.9
% Cryst. $^{(2)}$	180	170	125	145	175
% Shift	15	10	15	15	0
Na, Wt. % $^{(3)}$		0.26			

TABLE 1 (cont.)

Analyses of Products

Example Number	2	3	4	5	6
Calcination Condition	Before Treatment with Solution	After Treatment with 1 Normal NH_4Cl (¹)	After Treatment with 1 Normal HCl (¹)	After Treatment with 1 Normal $\text{Al}_2(\text{SO}_4)_3$ (¹)	After Treatment with 0.26 Normal $\text{Al}_2(\text{SO}_4)_3$ (¹)
1100° F., 1 Hr., in Steam, Atmospheric Pressure					
RE_2O_3 , Wt. %	26.5	26.6	21.6	24.3	26.0
Cyclohexane Ads., g/100 g	15.4	15.3	13.2	14.1	13.4
% Cryst. (²)	170	170	120	155	170
% Shift	10	10	40	10	0
Na, Wt. % (³)		0.26			
Surface Area m^2/gm	565				
1400° F., 1 Hr., in Steam, Atmospheric Pressure					
RE_2O_3 , Wt. %	26.5	25.1	16.9	22.8	25.0
Cyclohexane Ads., g/100 g	14.1	14.3	11	14.1	12.7
% Cryst. (²)	155	160	95	125	160
% Shift	55	40	50	40	10
Na, Wt. % (³)		0.22			0.14
1500° F., 1 Hr., in Steam, Atmospheric Pressure					
RE_2O_3 , Wt. %	26.5	26.7	19.1	24.4	26.3
Cyclohexane Ads., g/100 g	0.4	0.2	2.6	1.0	0.4
% Cryst. (²)	1.4	1.7	1.5	1.8	1.6
% Shift					
Na, Wt. % (³)		1.3			

(¹) Sample dried at 650° F. before analysis.(²) Crystallinity relative to standard. (The standard was sodium zeolite X which had been exchanged to 1.0 wt. % Na as described in Example 1. The RE_2O_3 content was 26.8 wt. %. The product was washed, dried, and calcined 2 hours at 600° F.)(³) Sodium analysis is on an ignited basis. Ignition at 1100° C

Fixation of Rare Earth Cations

Calcination at 650°F and higher temperatures also fixes the rare earth cations in the structure making them difficult to exchange. This is shown in Figure 3 and in Examples 3—6.

Ammonium chloride solution did not exchange any rare earth cations in REX samples calcined above 650°F. Aluminum sulfate solutions and hydrochloric acid solutions did extract some rare earth ions, even from calcined samples.

The amorphous sample (calcined at 1500°F) responded the same way as the crystalline samples to rare earth extraction by each of the solutions. The more dilute 0.26 normal aluminum sulfate solution extracted less rare earth than the 1 normal aluminum sulfate solution. Thus, calcined rare earth faujasite can be contacted by dilute salt and acid solutions without exchanging rare earth ions.

Crystal Stability to Acid Solutions

Calcined rare earth faujasite retains its crystallinity after contact with dilute dilute acid solutions. In contrast, sodium X is rendered completely amorphous by the same treatments. Uncalcined rare earth faujasite is intermediate between sodium X and calcined rare earth X.

Retention of crystallinity after contact with various acid solutions and ammonium chloride solution is shown in Figure 4 and in Examples 3—6. The 1N hydrochloric acid and $Al_2(SO_4)_3$ solutions destroy rare earth X crystals calcined below 650°F. More dilute aluminum sulfate solutions cause less destruction.

The stability of a crystalline aluminosilicate, having a 2.5 silica-to-alumina molar ratio, to acid solutions is entirely unexpected. Resistance to acids is usually associated with a silica to alumina molar ratio of above 5.0. The above results show that fixed cations can also impart acid stability to a zeolite.

When more than 50% of the rare earth ions were extracted by aluminum or hydrogen ion exchange no significant amount of crystallinity was preserved.

EXAMPLES 7—8

These examples show that very low sodium levels can be obtained by multiple calcinations when each calcination is followed by an ion exchange step. The sodium removal from two samples is compared below. Both samples (made in accordance with the method of Example 1) were calcined in steam at 1100°F for one hour, then exchanged twice. One sample (Example 8) was given an additional calcination in air between the two exchanges.

	Example 7	Example 8
Sodium Content, wt. %, After 1st Exchange With 1 Normal $CeCl_3$ Solution	.26	.26
Sodium Content, 25%, After 2nd Exchange With 1 Normal $CeCl_3$ Solution	.09	.03

In Example 8, wherein the sample was calcined between the two ion exchange steps, there resulted a lower sodium content. After each calcination, the sodium and rare earth ions seem to have been redistributed within crystalline positions, making some of the remaining sodium ions more exchangeable after each calcination.

EXAMPLES 9—10

These examples show that a rare earth faujasite which has been heated (calcined) can be flash dried without destruction of crystallinity.

One of the problems in the manufacture of fluid catalysts was loss in crystallinity of the uncalcined REX component during spray drying. Two samples of REX, each made in accordance with the method of Example 1, were dropped on a hot plate preheated to 1400°F. Time of contact of REX with the plate was 30 seconds. One sample had not been calcined. The other sample had been calcined at 1100°F as described previously. Both were water soaked and then equilibrated for 4 days in ambient air. The results of flash drying these materials at 1400°F were as follows:

	Example 9 Uncalcined REX	Example 10 Calcined REX
Crystallinity Before Flash Drying:	100%	100%
Crystallinity After Flash Drying:	75%	95%

The foregoing shows that crystal structure is more stable in flash drying when rare earth faujasite is first calcined.

EXAMPLES 11—12

5 These examples show that a rare earth faujasite (REX) that has not been subjected to heat treatment will, when exchanged with an aluminum sulfate solution, show a substantial loss in crystallinity, whereas a similar product which has been heat treated loses only a small portion of its crystallinity upon such aluminum sulfate treatment. 5

10 Samples of the material made as described in Example 1 were exchanged with (1) aqueous rare earth chloride and (2) aqueous aluminum sulfate under the conditions described in the Table below. Additional samples were first heated (calcined) for 12 hours at 1100°F., and were then subjected to the same exchange treatments. The crystallinity was measured by cyclohexane adsorption capacity and, in certain instances, also by X-ray crystallinity determinations. The data were as follows: 10

TABLE 2

Treatment No.	Treating Solution*	Example 11 REX of Example 1		Example 12 REX of Example 1, heated (calcined) at 1100° F. for 12 hours	
		Cyclohexane Absorption, wt. %	X-Ray Crystallinity Relative to Product from Treatment No. 1	Cyclohexane Adsorption, wt. %	X-Ray Crystallinity Relative to Product from Treatment No. 1
1	2 wt. % Rare earth chloride	15.8	100%	14.4	100%
2	2 wt. % $\text{Al}_2(\text{SO}_4)_3$	8.1	20%	14.5	90%

* 1000 ml of solution contacted with 40 gms of REX, dry basis, for 16 hours.

The foregoing shows that whereas the aluminum sulfate treatment markedly reduces the crystallinity (as measured by cyclohexane adsorption) of the uncalcined sample (Example 11), it does not significantly reduce the crystallinity of the calcined sample (Example 12).

EXAMPLE 13

This example illustrates the preparation of an active and selective cracking catalyst, which catalyst consists of a silica-alumina gel matrix containing dispersed therein rare earth aluminosilicate which, prior to its incorporation in the matrix, was subjected to calcination so as to "fix" the rare earth cations in the aluminosilicate.

One pound of rare earth faujasite made as described in Example 1 was heated (calcined) for 12 hours at 1100°F. The calcined powder was then added to 6.25 pounds of water to form a slurry. To this was added 13.9 pounds of sodium silicate and 7.02 pounds of water, with constant stirring. An acid solution was then prepared by mixing 28.55 pounds of water, 2.12 pounds of $\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, and 0.97 pound of 96.7 wt. % H_2SO_4 . The silicate and the acid solution were mixed continuously through a nozzle adding 492 cc. per minute of the silicate solution at 67°F. to 390 cc. per minute of the acid solution at 42°F. to form a hydrogel having a pH of 8.5 which gelled to a firm hydrogel in 1.9 seconds at 63°F. The hydrogel was then formed into a bead in a conventional manner and was treated with an equal volume of fresh 2

weight per cent aluminum sulfate solution, every two hours, for a total of 12 hours. Any residual sodium was scavenged from the hydrogel by a single 2 hour treatment with a 1% ammonium sulfate solution. The hydrogel was then washed free of sulfate ions, dried, calcined 3 hours in air at 1300°F., and steamed at 1200°F. for 24 hours with 15 psig steam.

A second catalyst (control) was made in similar fashion, however the rare earth faujasite was not calcined prior to its incorporation into the matrix.

The catalyst made utilizing the calcined REX gave a 67% conversion, whereas the catalyst made from uncalcined REX gave a conversion of only 39%.

EXAMPLE 14

This example shows the effect of a variety of base exchange solutions upon rare earth aluminosilicate fines which had initially been calcined.

Rare earth aluminosilicate fines in the form of a wet cake (55 wt. % solids) were prepared as described in Example 1. These fines contained 1.3 wt. % Na on a bone dry basis. The fines were divided into two portions, one of which was not subjected to calcination the other of which was calcined by heating for 12 hours at 1100°F. (until a residual moisture content* of 2% by weight was obtained). Thereafter, each of the foregoing portions was divided into separate samples, and each such sample was subjected to base exchange with the various solutions set forth in Table 3. In each instance, 40 grams of REX were placed in 1000 ml of solution and stirred intermittently for 24 hours.

$$* \text{ Moisture Content} = \frac{\left(\begin{array}{c} \text{Weight lost upon} \\ \text{calcining at a given} \\ \text{temperature for 1 hour} \end{array} \right) - \left(\begin{array}{c} \text{Weight lost upon} \\ \text{calcining at} \\ \text{1800°F. for 1 hour} \end{array} \right)}{\text{Weight lost upon calcining at 1800° F. for 1 hour}}$$

TABLE 3

Wet Fines Cake			Fines Calcined 12 Hrs. at 1100° F.		
Wt. % Na in Product	Cyc. hex ads. % wt.	Relative Crystallinity by Cyclohexane Adsorption	Wt. % Na in Product	Cyc. hex ads. % wt.	Relative Crystallinity by Cyclohexane Adsorption
Water	0.7	15.8	0.7	14.3	100%
2% Rare Earth Chloride Solution	0.6	15.8	0.07	14.4	100%
2% Calcium Chloride Solution			0.07		
2% Aluminum Sulfate Solution	8.1	51%		14.5	100%
2% Aluminum Nitrate Solution	13.6	86%	0.04	14.3	100%

Considering Table 3, it will be noted that in every instance the rare earth aluminosilicate fines which had initially been calcined showed a residual sodium content, after base exchange, of less than 0.1 weight per cent, whereas the fines which had not been so calcined showed a residual sodium content after base exchange of 0.5 to 0.6 wt. per cent.

EXAMPLE 15

Crystalline sodium aluminosilicate of the Y-type was prepared from the following two solutions:

- | | | |
|----|---|----|
| 5 | | |
| 10 | A. Silica Solution | 10 |
| | 1551 cc (1870 grams) of colloidal silica containing 0.361 gram SiO ₂ per cc | |
| | B. Sodium Aluminate Solution | |
| 15 | 75 grams NaAlO ₂ (41.7 weight per cent Al ₂ O ₃ ,
30 weight per cent Na ₂ O) | |
| | 330 grams NaOH (77.5 per cent by weight Na ₂ O) | 15 |
| | 1345 cc H ₂ O | |

The above solutions were mixed at a temperature of about 80°F. by pouring solution B into solution A. The resulting mixture was agitated vigorously for approximately one-half an hour to form a slurry, which slurry was then heat treated at a temperature of 200°F. for 42 hours. The solid material present was thereafter separated from the supernatant liquid by filtration. The filter cake obtained was washed with one volume of water per volume of initial slurry in order to remove the free caustic. At this point the cake was 73.3% solids, the solids containing 10.0 wt. % Na.

The Y-zeolite, prepared as previously indicated, was base exchanged with an aqueous solution containing 4 wt. % of mixed rare earth metal chloride having the following composition: 1.57 per cent cerium chloride, 0.83 per cent lanthanum chloride, 0.17 per cent praseodymium chloride, 0.58 per cent neodymium chloride and traces of samarium chloride, gadolinium chloride and other rare earth metal chlorides (1.5 g RECl₃/g fines). Base exchange was carried out continuously for 2 hours at 180°F. The base exchanged material was then washed free of chloride, and dried at 250°F.

The composition so obtained had a sodium content of 2.8 weight per cent and a rare earth metal oxide content of 14.6 wt. %.

EXAMPLE 16

This example utilizes rare earth aluminosilicate fines of the Y-type (REY) prepared as described in Example 15. As is illustrated in the present example, residual sodium present in such rare earth aluminosilicate fines is much more easily removed by rare earth exchange when such fines are first calcined and partially dehydrated.

The rare earth aluminosilicate fines of Example 15 were calcined by heating in steam for two hours at varying temperatures as shown in Table 4.

Thereafter the fines were exchanged once for two hours at 180°F. with a 4% RECl₃·6H₂O solution (1.5 grams of rare earth chloride per gram of fines), followed by filtering and washing the filter cake free of chloride ion.

Table 4 shows that whereas with no initial calcination, rare earth exchange resulted in a residual sodium content of 2.5 per cent by weight, with a calcination of the fines followed by rare earth exchange, the residual sodium content was reduced to from about 0.4 to 0.7 weight per cent.

After the foregoing rare earth exchange, the fines were again subjected to steaming for two hours at the temperatures indicated in Table 4, followed by a second rare earth exchange, filtering, washing, and drying. The results are shown in Table 4. It will be noted that a second calcination followed by a second rare earth exchange further reduced the residual sodium content. Thus, whereas the "control" showed a residual sodium content of 2.1 weight per cent, those samples which were steamed and then rare earth exchanged showed residual sodium contents of from about 0.06 to 0.2 weight per cent.

TABLE 4

Preparation of Low Sodium (<0.1% wt.) Rare Earth Aluminosilicate Fines (REY) from Sodium Aluminosilicate Fines (NaY)
(dry sodium aluminosilicate fines 73.3% solids; 70/100:cryst/shift; 10.0% Na; 19.1 cyclo C₆₀ ads.)

Exchange Powdered Fines with 4% RECl ₃ ·6H ₂ O Sol'n for 2 Hours at 180° F., Filter and Wash Cl- Free Dry at 250° F. (1.5 g RECl ₃ ·6H ₂ O/g Sodium Aluminosilicate Fines) Na = 2.8%			
	Treat 2 hr. at 650° F. 100% steam, 0 psig	Treat 2 hr. at 1300° F. 100% steam, 0 psig	Treat 2 hr. at 950° F. 100% steam, 0 psig, results in 0.8 wt. % H ₂ O
Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Na = 2.5%	Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Na = 0.69%	Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Na = 0.55%	Exch. 2 once hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash RE ₂ O ₃ = 19.4% Na = 0.39%
Air Temp. Sample	Treat 2 hr. at 650° F. 100% steam, 0 psig	Treat 2 hr. at 1300° F. 100% steam, 0 psig	Treat 2 hr. at 950° F. 100% steam, p psig, results in 0.8 wt. % H ₂ O
Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Dry at 250° F. Na = 2.1%	Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Dry at 250° F. Na = 0.21%	Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Dry at 250° F. Na = 0.15%	Exch. once 2 hr. 180° F. with 4% RECl ₃ ·6H ₂ O (1.5 g RECl ₃ ·6H ₂ O/g REY) Filter, Wash Dry at 250° F. Na = 0.06%

EXAMPLE 16

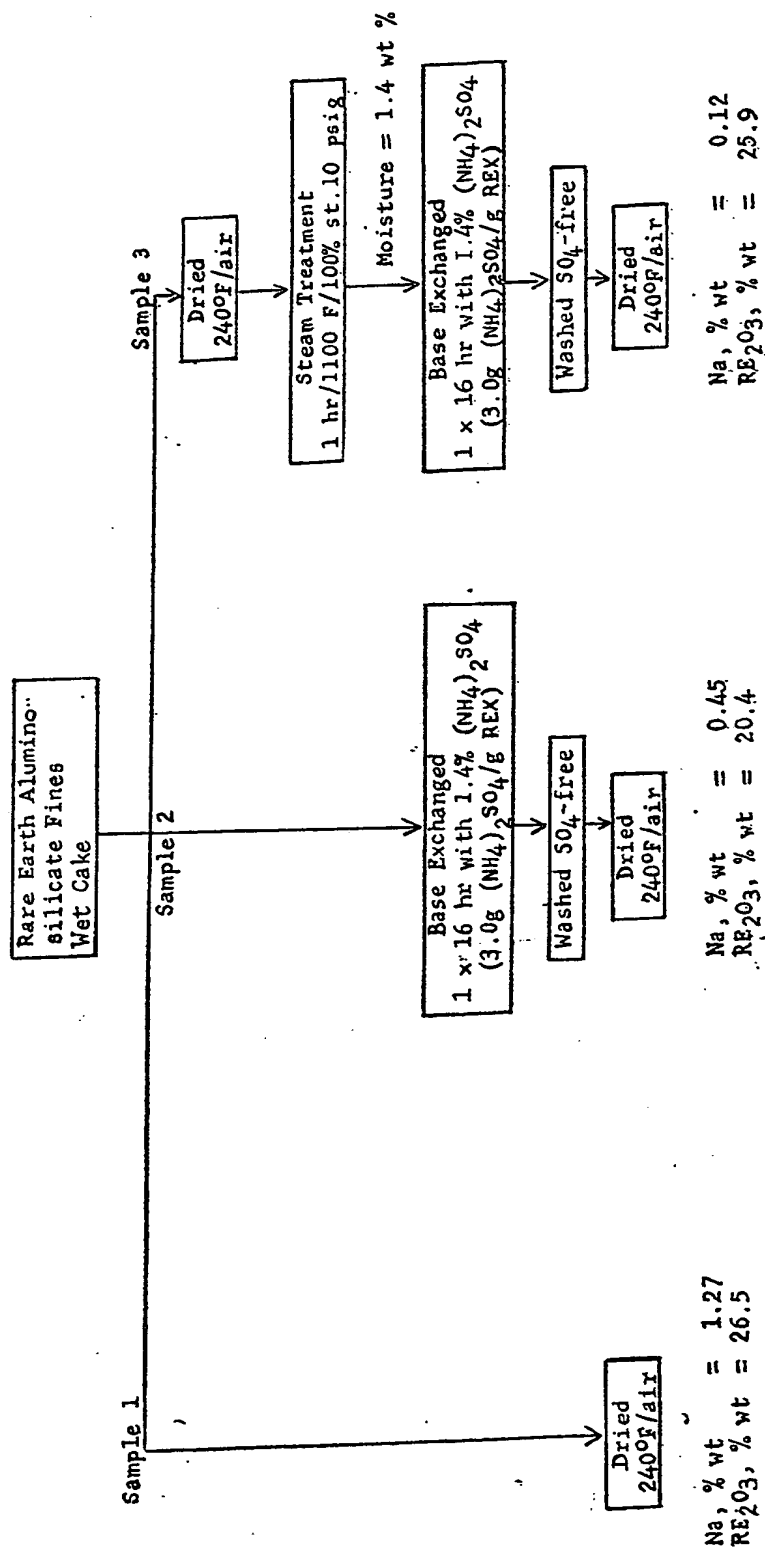
This example illustrates the effect of calcination of rare earth aluminosilicate (REX) fines upon subsequent base exchange treatment with an ammonium salt.

5 A wet cake of rare earth aluminosilicate fines made as described in Example 1, this wet cake containing 46.2 per cent by weight of water, was divided into three portions. The first was dried in air at 240°F., and then slugged into a $\frac{1}{2}$ " diameter sample. The second was base exchanged for 16 hours with a 1.4 weight per cent ammonium sulfate solution (3 grams of ammonium sulfate per gram of fines), there-
10 after washed free of sulfate ion, dried in air at 240°F., and slugged to a $\frac{1}{2}$ " diameter sample. The third was first dried in air at 240°F. to a residual moisture content of 8.7 weight per cent, and thereafter was partially dehydrated by treating for one hour at 1100°F. with 100 per cent steam at 10 psig to yield a product having a residual moisture content of 1.4 weight per cent. Thereafter, the partially dehydrated fines were base exchanged with ammonium sulfate solution, washed, dried, and slugged in
15 the same manner as described with respect to the second portion.

Table 5 tabulates the treating conditions and the resulting properties. It will be noted that Sample 1, wherein the fines were merely dried, showed a residual sodium content of 1.27 weight per cent and a rare earth content of 26.5 weight per cent. Sample 2, which was subjected to base exchange with ammonium sulfate, showed a
20 residual sodium content of 0.45 weight per cent. However, the base exchange not only removed sodium, but also removed rare earth, for the residual rare earth content was only 20.4 weight per cent. In contrast, Sample 3, which was first steamed to a residual moisture content of 1.4 weight per cent and thereafter was base exchanged, showed a residual sodium content of only 0.12 weight per cent. Moreover, Sample 3 shows
25 a particularly desirable result in that although the ammonium sulfate base exchange was most effective in reducing the sodium content, it did *not* appreciably reduce the rare earth content, which remained at 25.9 weight per cent as compared to 26.5 weight per cent for the "control" which had not been subjected to any base exchange.

Table 6 sets forth additional data relating to each of the foregoing samples. It
30 will be noted that Sample 3 shows superior conversion and superior hexane cracking as compared to Samples 1 to 2.

Table 5
Steam and Thermal Stability of Rare Earth Aluminosilicate Fines (REX)



EXAMPLE 17

Rare earth aluminosilicate fines were prepared as described in Example 1. These fines had a residual sodium content of 0.4 weight per cent. The fines were dried at 240°F. Thereafter, the fines were divided into five portions. The first (Sample 1), which served as a control, was incorporated by mixing in a water slurry of a silica-alumina cogel matrix. The remaining four portions were each subjected to calcination by heating for two hours at 650°F. in air. The first of these portions (Sample 2) was then incorporated in a silica-alumina cogel matrix as described above. The remaining three portions (Samples 3—5) were slugged to samples $\frac{1}{2}$ inch in diameter, heated for two hours at 650°F. in air, and then steamed for varying times at 1200°F. with 100 per cent steam at varying pressures, and then incorporated in a silica-alumina cogel matrix.

Each of the above five samples was then tempered for two hours at 650°F. in air, slugged to $\frac{1}{2}$ inch diameter and the relative crystallinity and rare earth content (expressed as rare earth oxides) was determined. Referring to Table 7, it will be noted that Sample 1, the fines of which were not subjected to initial partial dehydration, showed a relative crystallinity of 0.7 and a rare earth content of 1.16. In contrast, each of Samples 2—5, wherein the fines had been subjected to partial dehydration, showed relative crystallinities in excess of 10 and rare earth contents of roughly 2 per cent by weight.

The five samples were then tested for steam stability by steam treatment for 24 hours at 1200°F. with 100% steam at 15 psig and thereafter, the relative crystallinity was measured. The control showed a relative crystallinity of 0.7. The crystallinity of Sample 2 was 5.5 and that of Samples 3—5 was 10 or greater.

Each of the foregoing catalysts was tested for catalytic activity. Samples 2—5 showed conversions of between 45 and 53.2%, as compared to a 29.6% conversion for Sample 1. Moreover, the gasoline yield for each of Samples 2—5 was markedly superior to that for the catalyst of Sample 1.

TABLE 6
Steam Stability
Rare Earth Aluminosilicate Fines

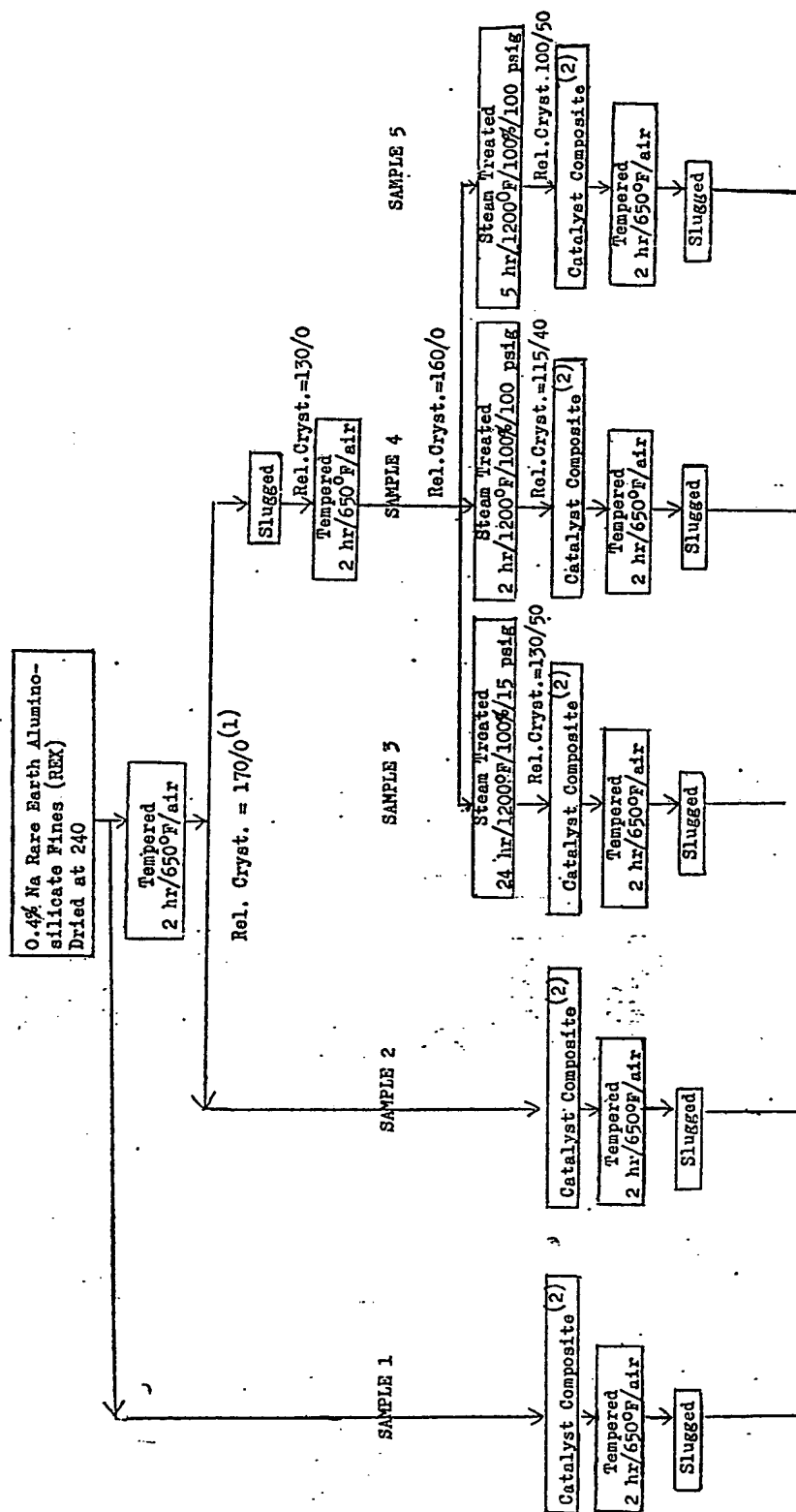
Sample 1			Sample 2			Sample 3		
1.27% wt. Na			0.45% wt. Na			0.12% wt. Na		
Before Test	After Test	% Loss	Before Test	After Test	% Loss	Before Test	After Test	% Loss
(1)	(2)		(1)	(2)		(1)	(2)	
52.0	39.5	25	50.8	15.2	70	54.6	53.2	5
Conversion in cracking Test*, % Vol.								

(1) Steam treated 24 hrs./1200°F/100% steam/15 psig.

(2) Standard steam stability test (5 hr/1200°F/100% steam/100 psig.)

* 900°F; LHSV = 16; 0.38 Catalyst: Oil Ratio (C/O).

Table 7



(Table 7 cont.)

Rel.Cryst. = 0.7 RE_{2O_3} = 1.16 Steam Treated 24 hr/1200°F/100%/15 psig	Rel.Cryst. = 10.5 RE_{2O_3} = 2.10 Steam Treated 24 hr/1200°F/100%/15 psig	Rel.Cryst. = 13.6 RE_{2O_3} = 1.92 Steam Treated 24 hr/1200°F/100%/15 psig	Rel.Cryst. = 11.4 RE_{2O_3} = 1.85 $Na = 7.13$ Steam Treated 24 hr/1200°F/100%/15 psig	Rel.Cryst. = 11.8 RE_{2O_3} = 1.79 Steam Treated 24 hr/1200°F/100%/15 psig
Rel.Cryst. 0.7 Cracking Test Conv. 29.6 Gaso. 24.9 C ₄ 's 5.4 Dry Gas 4.0 Coke 0.7	Rel.Cryst. 5.5 Cracking Test Conv. 46.6 Gaso. 38.6 C ₄ 's 9.6 Dry Gas 5.6 Coke 0.9	Rel.Cryst. 15.5 Cracking Test Conv. 53.2 Gaso. 44.6 C ₄ 's 11.1 Dry Gas 6.0 Coke 0.9	Rel.Cryst. 10.1 Cracking Test Conv. 49.9 Gaso. 41.9 C ₄ 's 10.0 Dry Gas 5.4 Coke 1.0	Rel.Cryst. 10.0 Cracking Test Conv. 45.0 Gaso. 37.4 C ₄ 's 9.0 Dry Gas 5.3 Coke 1.1

(1) "XXX/XX" denotes relative crystallinity and shift, respectively.

(2) 7.5% wt rare earth aluminosilicate fines and 92.5% wt silica-alumina cogel matrix (90% SiO₂, 10% Al₂O₃)

(3) 900°F, 4.5 LHSV, and 1.3 O/O

Percentage crystallinity is determined by X-ray diffraction techniques. Relative crystallinity is the ratio of the degree of crystallinity detected by such techniques, of the samples used in Table 7 to a standard. "Shift" gives a measure of the apportionment between zeolite X and zeolite Y of the contents of a sample.

5

EXAMPLE 18

5

This example shows the effect of heating time upon residual alkali metal content after ion exchange.

10

10 grams of REX made by the procedure of Example 1, and containing 1.3 wt. % residual sodium, were agitated for 24 hours with 100 ml of 1 Normal NH_4Cl solution. Prior to such treatment, each 10 gram sample had been subjected to heating at 250°F. for the time indicated in Table 8.

10

TABLE 8

Time REX was held at 250°F. in oven air atmosphere, Hrs.	Sodium Content after NH_4Cl exchange, Wt. % Na on dry basis	Moisture Content*, gm H_2O per 100 gm dry zeolite
0	1.30	51
1	0.83	22
4	0.62	17
24	0.43	15
72	0.43	15

* Determined by ignition loss at 1100° C. for 1 hour.

15

A residence time in excess of 24 hours followed by ion exchange did not further reduce residual sodium content below 0.43 wt. %. It should be noted, however, that by use of higher temperatures followed by ion exchange, the residual sodium content can be reduced well below 0.43 wt. %. (See, e.g., Table 1, Example 3).

15

EXAMPLES 19—28

20

These examples describe the preparation of starting zeolite materials. (Examples 29—45 describe the results of exchanging the zeolite of Examples 19—28, both calcined and uncalcined, with various solutions).

20

EXAMPLE 19

25

Calcium offretite. Synthetic offretite (zeolite T) was prepared as described in Example 1 of U.S. Patent 2,950,952. The washed product was stored as a wet filter cake. The mole composition of this synthetic offretite on a dry basis was found to be $0.35 \text{ Na}_2\text{O} \cdot 0.91 \text{ K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 7.27 \text{ SiO}_2$. The wet cake contained 34% solids, 66% water.

25

30

98 grams of this wet offretite filter cake were given three batch exchanges with 800 grams of 5% CaCl_2 solution for each exchange. Exchange temperature was 195°F and time of contact for each exchange was 8 hours. The cake was washed with water between exchanges. After the last exchange the cake was stored as washed, wet cake.

30

EXAMPLE 20

Lanthanum offretite. The same procedure was followed as described in Example 19 except that 3.5% wt LaCl_3 solution was used in place of 5% wt CaCl_2 solution.

EXAMPLE 21

Sodium offretite. The same procedure was followed as described in Example 19 except that 10% wt NaCl solution was used in place of the 5% wt CaCl_2 solution.

EXAMPLE 22

5 Ferrous ammonium Y. Zeolite sodium Y was prepared as described in U.S. Patent 3,130,007. The washed, wet filter cake, containing 40% solids, 60% water, had the following mole composition on a bone dry basis: $1.02\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5.6\text{SiO}_2$.

10 Seventy-five grams of wet cake were given 10 batch exchange treatments with 300 grams of 10% ferrous ammonium sulfate (formula weight 392.16) solution per exchange. Each batch contact was for 12 hours at 195°F . After the last exchange the cake was washed and dried for 16 hours at 250°F . The sodium content of the ferrous ammonium Y was found to be 1.8% wt, as Na.

EXAMPLE 23

15 Chromium Y was prepared by the procedure given in Example 22, except that 10% chromic chloride hydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) of pH 1.9, was used in place of the ferrous ammonium sulfate solution. The dried chromic Y had a sodium content (as Na) of 1.5% wt.

EXAMPLE 24

20 Iron mordenite. Synthetic sodium mordenite, designated as Zeolon Na, was obtained from the Norton Company. The mole composition on a bone dry basis was $0.8\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8.5\text{SiO}_2$. Moisture content was 15%.

25 Seventy-five grams of this zeolite were ion exchanged by the procedure described in Example 22, except that 5% ferric chloride (FeCl_3) solution, pH 1.3, was used in place of the ferrous ammonium sulfate solution. The dried product contained 1.9% wt sodium (as Na) on a bone dry basis.

EXAMPLE 25

30 Chromium mordenite. The chromium mordenite was prepared by the same procedure as described in Example 24, except that 10% chromic chloride (CrCl_3) solution, pH 1.9, was used instead of the ferric chloride solution. The sodium content of the final product on a bone dry basis was 2.9% wt as Na.

EXAMPLE 26

35 Lanthanum X. Sodium X was prepared as described in U.S. Patent 2,882,244. The washed filter cake had the following mole composition: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2$. The cake contained 55% solids, 45% water.

40 Four hundred grams of this wet cake were given six batch ion exchange contacts at 195°F with 1500 grams of 10% CaCl_2 solution per contact. The final water washed product was dried for 16 hours at 250°F . The product was calcium zeolite X, containing 0.2% wt Na on a dry basis.

45 Fifty grams of calcium zeolite X were given three batch contacts at 195°F using 740 grams of 3.5% LaCl_3 solution per contact. The cake was washed with water between exchanges. The final product was stored as washed wet filter cake.

EXAMPLE 27

50 Lanthanum mordenite. A sample of natural mordenite was analyzed and found to have the following composition as wt %: K=1.6; Na=3.55; SiO_2 =72.1; Al_2O_3 =15.7; Ca=2.45. 10.8 grams of this material were pulverized and contacted with 0.3N LaCl_3 solution for 1 hour at 400°F under the autogenous pressure of the solution. The sample was washed and dried. This product, lanthanum mordenite, had the following composition on bone dry % weight basis: K=1.06; Na=1.29; SiO_2 =72.6; Al_2O_3 =14.5; La_2O_3 =6.93; Ca=1.44. The moisture content of the product was 10%.

EXAMPLE 28

5 Twenty grams of calcium offretite, wet cake, made as described in Example 19, were mixed with 100 grams of 5.3% wt NH_4Cl aqueous solution. The slurry was stirred in a one-quart bottle for 2 hours at a temperature of 75°F. The solids were then filtered, washed, dried and analyzed for potassium. The potassium (K) content of the product on a dry basis was 3.3% wt. (See Table 9.) 5

EXAMPLE 29

10 Twenty grams of calcium offretite, wet cake, identical with that used in Example 28, were placed in a crucible. The covered crucible was calcined for 3 hours at 1000°F. 10.6 grams of water were driven off by the calcination. The total quantity of calcined solids, 9.4 grams, were mixed with 10.6 grams of water and 100 grams of 5.3% wt NH_4Cl solution. The sample was stirred in a one-quart bottle for 2 hours at a temperature of 75°F. The solids were then filtered, washed, dried and analyzed for potassium. 15 The potassium (K) content of the product on a dry basis was 2.1% wt. Comparison of Examples 28 and 29 shows that the residual potassium in the calcined sample is more readily exchangeable than the residual potassium in the uncalcined sample. (See Table 9.) 15

EXAMPLES 30—45

20 Using the starting materials set forth in Table 9, the ion exchange was carried out, either without a preceding calcination step (Examples 30, 32, 34, 36, 38, 40, 42, and 44 which are included as comparative Examples), or following calcination (Examples 31, 33, 35, 37, 39, 41, 43, and 45). In all instances the ion exchange was carried out using a two hour contact with the exchange solution. The particular exchange solution used and the results obtained are set forth in Table 9. In every instance, calcination rendered the residual cation more exchangeable. 25

Table 9

Ion Exchange of Calcined and Uncalcined Crystalline Zeolite									
Example No.	Starting Material	Principal Residual Cation Present	Principal Residual Cation	Heat Treatment	Ion Exchange Solution, Grams				Analysis for Principal Residual Cation in Exchanged Zeolite wt % on bone dry basis
					Gms of Material Used*	10% wt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ soln, pH = 2.5	10% wt FeCl_3 soln, pH = 0.5	5.3% wt NaCl soln	
28	Calcium Offretite (Ex. 19)	K	-	{ Wet cake never dried	20.0		100	-	{ K 3.3
29				{ Calcined 3 hours at 1000°F	9.4		100	10.6	{ K 2.1
30	Lanthanum Offretite (Ex. 20)	K	-	{ Wet cake never dried	20.0		100	-	{ K 2.9
31				{ Calcined 3 hours at 1000°F	7.8		100	12.2	{ K 2.2
32	Sodium Offretite (Ex. 21)	K	-	{ Wet cake never dried	15.0		100	-	{ K 3.1
33				{ Calcined 3 hours at 1000°F	6.1		100	8.9	{ K 2.6
34	Ferrous Ammonium Y (Ex. 22)	Na	1.8	{ Dried 16 hours at 250°F	10.0		100	-	{ Na 1.7
35				{ Calcined 3 hours at 1000°F	7.5		100	2.5	{ Na 0.6
36	Chromium Y (Ex. 23)	Na	1.8	{ Dried 16 hours at 250°F	10.0	100		-	{ Na 1.8
37				{ Calcined 3 hours at 1000°F	7.7	100		2.3	{ Na 0.5
38	Iron Mordenite (Ex. 24)	Na	1.8	{ Dried 16 hours at 250°F	10.0	100		-	{ Na 1.6
39				{ Calcined 3 hours at 1000°F	8.8	100		1.2	{ Na 0.9
40	Chromium Mordenite (Ex. 25)	Na	2.9	{ Dried 16 hours at 250°F	10.0	100		-	{ Na 2.9
41				{ Calcined 3 hours at 1000°F	8.9	100		1.1	{ Na 2.5
42	Lanthanum X (Ex. 26)	Ca	-	{ Wet cake never dried	20.0		100	-	{ Ca 1.5
43				{ Calcined 3 hours at 1000°F	9.3		100	10.7	{ Ca 0.9
44	Lanthanum Mordenite (Ex. 27)	K, Ca, Na	-	{ Dried 16 hours at 250°F	6.0		100	-	{ Na 1.0
45				{ Calcined 3 hours at 1000°F	5.4		100	0.6	{ Na 0.5

* Wet and calcined samples of each zeolite contain the same weight of bone dry solids.

WHAT WE CLAIM IS:—

1. A method of preparing a crystalline aluminosilicate for use as a catalyst, comprising heating an aluminosilicate containing mono- and/or divalent cations to a temperature in the range 150 to 1700°F for a time sufficient to reduce the moisture content of the aluminosilicate to less than 90% of saturation and thereafter subjecting the aluminosilicate to base-exchange to reduce the content of said mono- and/or divalent cations to less than 80% of their content prior to said base-exchange. 5
2. A method according to Claim 1 wherein the minimum temperature to which the aluminosilicate is heated is 250°F.
3. A method according to Claim 2 wherein the temperature is in the range 1200 to 1400°F. 10
4. A method according to any one of Claims 1 to 3 wherein the moisture content of the aluminosilicate is reduced by the heating to less than 70% of saturation.
5. A method according to any one of Claims 1 to 4 wherein the moisture content of the aluminosilicate is reduced by the heating to less than 20% of saturation. 15
6. A method according to any one of Claims 1 to 5 wherein the aluminosilicate is subjected to base-exchange with trivalent metal cations.
7. A method according to Claim 6 in which the trivalent metal cations are rare earth cations or yttrium cations.
8. A method according to any one of Claims 1 to 7 wherein said monovalent cations are alkali metal cations. 20
9. A method according to Claim 8 wherein the alkali metal cations are sodium cations.
10. A method according to Claim 9 wherein the sodium cations have resisted removal in a prior base-exchange. 25
11. A method according to Claim 10 wherein the prior base-exchange replaced sodium ions by rare earth ions.
12. A method according to any one of Claims 9 to 11 wherein the base-exchange subsequent to the heating replaces sodium ions by rare earth ions.
13. A method according to any one of Claims 1 to 12 wherein the aluminosilicate contains trivalent cations, in addition to the mono- and/or divalent cations, before being heated. 30
14. A method according to any one of Claims 1 to 13 wherein a substantial proportion of the cations in the aluminosilicate starting material are rare earth cations.
15. A method according to any preceding claim wherein the aluminosilicate is heated in an atmosphere of steam, air-steam, nitrogen, flue gas, oxygen or hydrogen. 35
16. A method according to any preceding claim wherein after the base-exchange subsequent to the heating, the aluminosilicate is once more subjected to the heating followed by the base-exchange.
17. A method according to any preceding claim wherein base-exchange of the aluminosilicate subsequent to heating reduces the alkali metal content of the aluminosilicate to a value within the range 0.03 to 0.2 weight per cent. 40
18. A method according to any of Claims 1 to 16 wherein the aluminosilicate subjected to base-exchange subsequent to heating is mixed with relatively catalytically inert material. 45
19. A method according to Claim 18 wherein the aluminosilicate subjected to heating is mixed with relatively catalytically inert material.
20. A method according to Claim 19 wherein the aluminosilicate subjected to base-exchange prior to heating is mixed with relatively catalytically inert material.
21. A method according to any preceding claim wherein after the final base-exchange the aluminosilicate is spray-dried. 50
22. A method of preparing a crystalline aluminosilicate by base-exchange subsequent to heating, substantially as described in any of Examples 2 to 18, 29, 31, 33, 35, 37, 39, 41, 43 and 45.
23. Crystalline aluminosilicates whenever prepared by the method claimed in any of Claims 1 to 22. 55
24. Hydrocarbon conversion catalysts comprising a crystalline aluminosilicate claimed in Claim 23.

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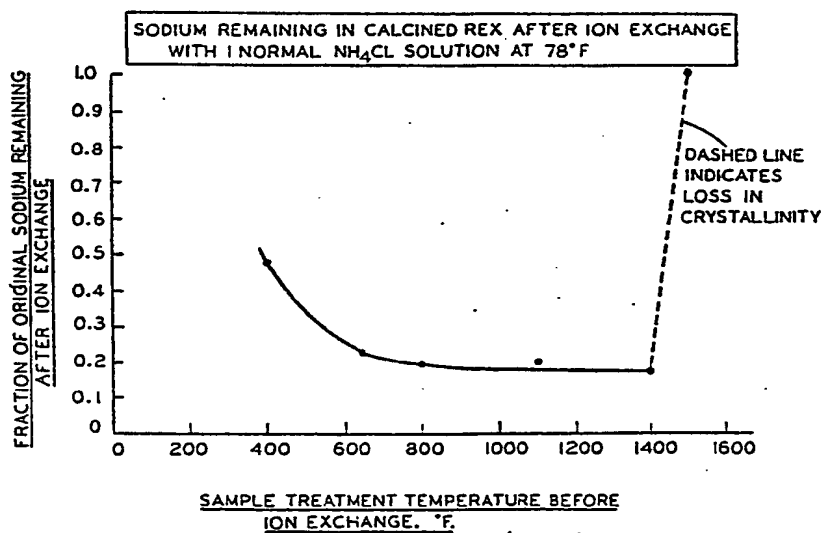
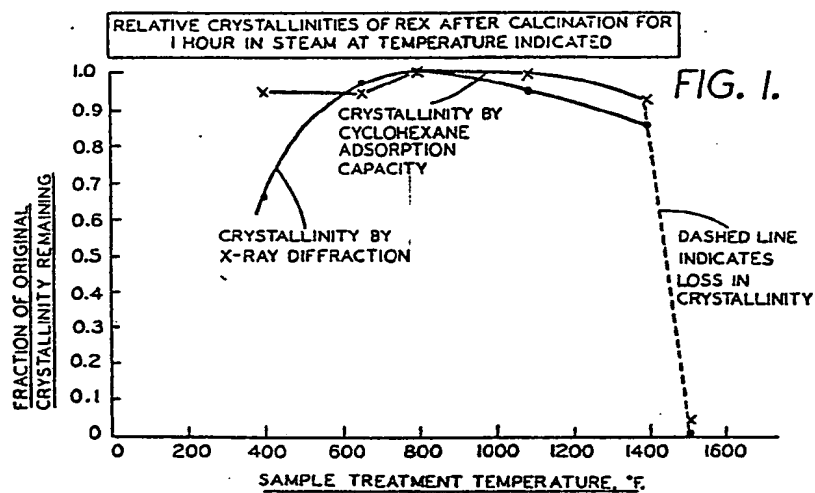


FIG. 2.

FIG. 3.

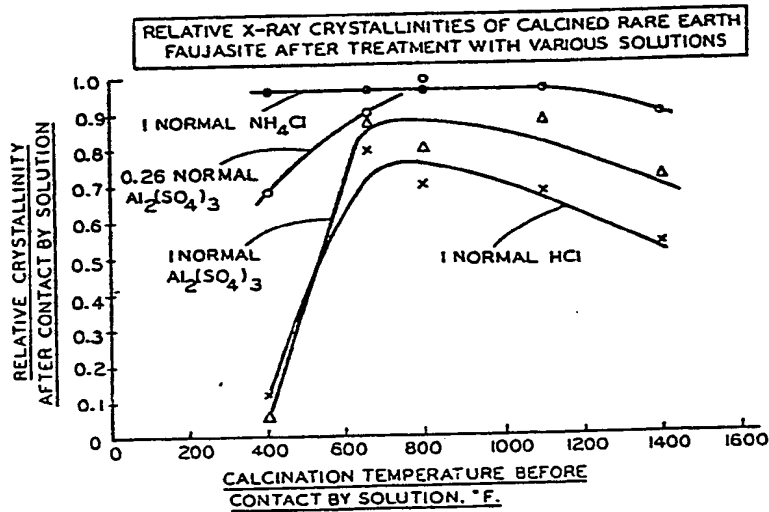
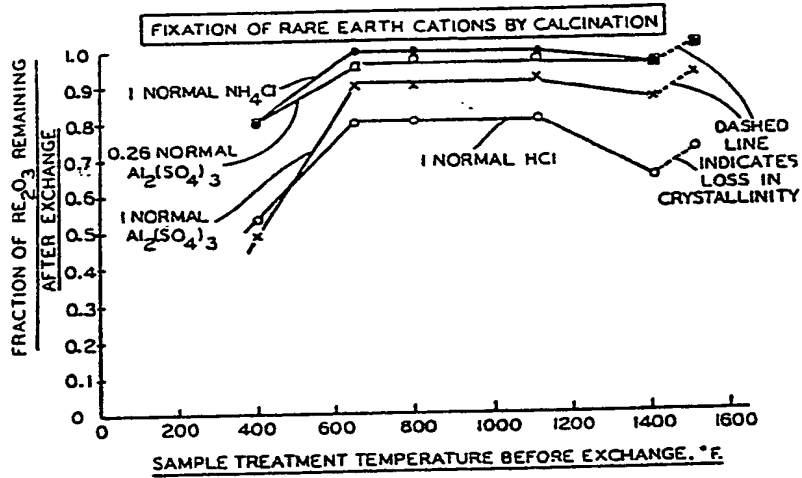
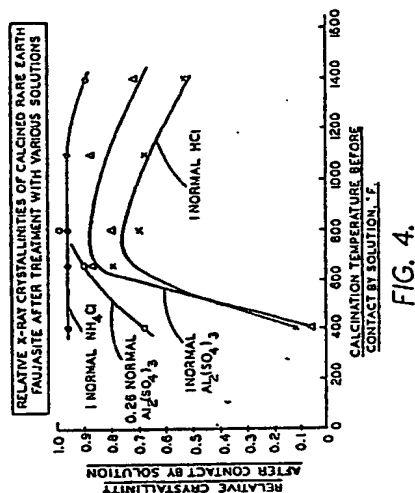
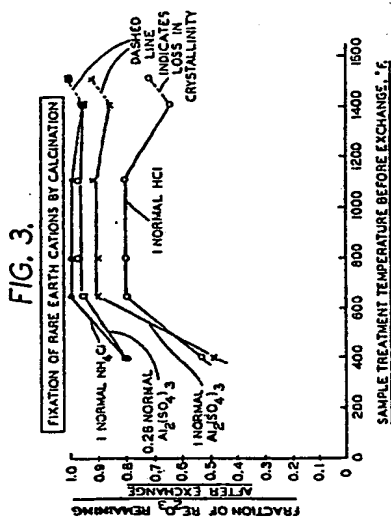
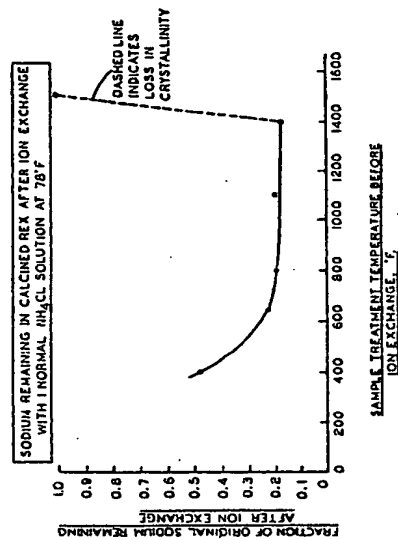
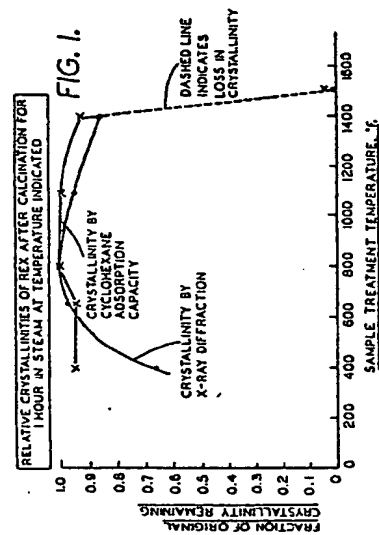


FIG. 4.



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